Solid-state NMR study of photocatalytic oxidation of acetaldehyde over the flame-made F-TiO₂ catalyst

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ABSTRACT

Solid-state ^{13}C high-power proton decoupling (HPDEC), cross-polarization (CP), and 2-dimensional (2D) ^{13}C-^{13}C homonuclear correlation NMR techniques were used to study the adsorption of acetaldehyde on the flame-made fluorinated TiO₂ (F-TiO₂) catalyst, subsequent photocatalytic oxidation, and complete photo-decomposition at the presence of oxygen under UV light irradiation. Crotonaldehyde is formed via the acid-catalyzed aldol condensation through the adsorption of acetaldehyde on the F-TiO₂ catalyst at room temperature without light illumination. At the presence of molecular oxygen as an electron acceptor, surface bonded acetaldehyde and crotonaldehyde are completely oxidized by the transient holes in the oxygen framework generated by UV light irradiation. This work provides clear evidence for the formation of crotonaldehyde, acetic acid, and formic acid, along with acetate and formate complexes. The identified surfaces complexes participate actively in the photocatalytic oxidation and do not play a significant role in the poisoning of the active sites, at least in such concentrations. The reaction pathways are therefore established.

1. Introduction

Heterogeneous photocatalysis has been widely studied to degrade organic pollutants both in gaseous and aqueous system [1,2]. It is also considered as a promising green route for organic synthesis [3]. Up to now, the photocatalytic oxidation (PCO) is one of the most studied reaction classes, particularly hydrocarbon oxidation into highly desirable oxygenates such as ketones, aldehydes and carboxylic acids [4]. In a typical photocatalytic oxidation, a semiconductor photocatalyst can be excited by UV–vis light followed by subsequent electron transfer to the catalyst surface, available for chemical reactions in heterogeneous photocatalytic process. Industrial processes for oxidation reactions have generally been conducted using stoichiometric amounts of heavy metal reagents such as Cr, Mn salts or V_2O_5 or moisture-sensitive oxidants. Among numerous semiconductor photocatalysts, titanium dioxide (TiO₂) is by far the most viable materials used in photocatalysis due to its high activity, good stability, low cost, and lack of toxicity [5].

In the TiO₂-based photocatalysis, catalytic reaction basically takes place on the surface of TiO₂. It is well accepted that the outer surface of TiO₂ is generally covered with a layer of hydroxyl groups (TiOH). To some extent, the nature of surface TiOH groups is governing the surface reaction that ensues. It has been evidenced that the bridging TiOH groups possess acidic properties, whilst the terminal TiOH groups are characteristic of base [6]. Our previous work demonstrates that the level of terminal TiOH groups on the TiO₂ surface is vital for defining the photocatalytic oxidation of acetaldehyde on the TiO₂ material. Low terminal TiOH content accounts for the high photocatalytic activity [7]. Instead of necessitating additional acid treatment of the surface, our recent work has found that the photocatalytic activity can be elevated simply by controlling the intrinsic distribution of native TiOH groups on the TiO₂ surface [8]. Evidenced by ^{1}H magic-angle spinning (MAS) nuclear magnetic resonance (NMR) results, the fluorinated TiO₂ (F-TiO₂) prepared by a simple one-step flame spray pyrolysis (FSP) shows a very low terminal TiOH content due to the exchange between surface TiOH and fluorine precursors during the FSP synthesis. It indicates that the F-TiO₂ mainly possesses acidic properties. This finding leads to an idea that the F-TiO₂ could be employed as a solid acid photocatalyst in acid-catalyzed reactions.

Previous studies have demonstrated that photocatalytic oxidation technology can successfully decompose many gas-phase

organics, but reaction pathways involved are not fully understood and particularly, the intermediates are often not identified if they do not leave the catalyst. Photocatalytic oxidation of aqueous-phase organics has been studied more extensively, and the mechanism may be quite different for the gas-phase reactions. In order to develop improved photocatalysts, more fundamental understanding of reaction pathways should be acquired. In turn, this knowledge necessitates identifying surface species and active sites on the most promising photocatalyst, fluorinated TiO2. Understanding the reaction mechanisms and identifying surface species during the photocatalytic oxidation of acetaldehyde are important because many organic pollutants that consist of two or more carbon reaction through an acetaldehyde intermediate. Idriss et al. have studied the reactions of acetaldehyde on oxidized and reduced TiO2 surface [9]. Infrared (IR) studies conducted by Singh et al. have observed the formation of 3-hydroxybutanal intermediate during adol condensation when acetaldehyde adsorbs onto TiO2 at the temperature range of 233–250 K [10]. Acetaldehyde condensation has been further reported over other metal oxides including silica supported magnesia and zirconia [11]. Topalian et al. have investigated the adsorption and photocatalytic oxidation of acetaldehyde on TiO2 and sulfate-modified TiO2 by in situ FT-IR spectroscopy [12]. Compared to the TiO2, the formation of intermediate products is impeded on the sulfate-modified TiO2.

Raftery's group has undertaken a number of in situ solid-state ^{13}C NMR studies on photocatalytic oxidation of acetone [13], ethanol [14], 2-propanol [15], and trichloroethylene [16] on different TiO2-based catalysts. solid-state ^{13}C NMR studies of acetaldehyde condensation on zeolite HZSM-5 by Haw's group reveals that crotonaldehyde product from acetaldehyde conversion on acidic zeolite H-ZSM-5 was observed at 353–393 K [17]. Biaglow et al. have studied the acid-catalyzed condensation of acetone and acetaldehyde on H-ZSM-5 by solid-state ^{13}C NMR spectroscopy [18]. Photo-induced acidic reactions between benzaldehyde or acetophenone and toluene in FAU type zeolites have been reported by Haw's group [19]. In the present work, solid-state ^{13}C high-power proton decoupling (HPDEC), cross-polarization (CP), and 2-dimensional (2D) ^{13}C-^{13}C homonuclear correlation NMR techniques were used to understand the adsorption of acetaldehyde on the surface of F-TiO2 synthesized by flame spray pyrolysis, subsequent photocatalytic oxidation and complete photo-decomposition at the presence of molecular oxygen under UV light irradiation.

2. Experimental

2.1. Preparation of F-TiO2

Titanium tetraisopropoxide (Aldrich, 97%), hexafluorobenzene (Aldrich, 99%), xylene (analytical grade, Univar), and acetonitrile (analytical grade, Fluka) were used as received. Fluorinated TiO2 materials were prepared by one-step flame spray pyrolysis (FSP). The experimental set-up used for FSP has been described in detail elsewhere [7]. In brief, flame-made F-TiO2 was prepared by dissolving titanium tetraisopropoxide and hexafluorobenzene in a 1:1 (vol%) mixture of acetonitrile/xylene. The resulting solution was filtered over a glass filter, fed to the flame through a syringe pump at 5 mL/min and dispersed by 5 L/min of O2 at 1.5 bar. The resulting spray was ignited by an annular supporting methane/oxygen flame (1.5/3.2 L/min) resulting in an approximately 6 cm long flame. Particles were collected on a cooled fiberglass filter (Whatmann GF6, 257 mm in diameter) by assistance of a vacuum pump (Alcatel SD series).

2.2. Adsorption of acetaldehyde

Before adsorption of 1, 2-^{13}C enriched acetaldehyde (Cambridge Isotope Laboratories, ^{13}C-enrichment 99%) on the F-TiO2, 200 mg of F-TiO2 catalyst filled in a glass tube (outer diameter of ca. 6 mm and length of ca. 180 mm) was previously outgassed with vacuum stopcocks connected to a vacuum line at 393 K for 1 h under a vacuum better than 10^{-2} pa to remove water molecules, and then cooled the sample to room temperature. Prior to the loading of 1, 2-^{13}C enriched acetaldehyde, several "freeze-pump-thaw" cycles were carried out to purify the acetaldehyde. Adsorption of acetaldehyde (50 μmol) and oxygen (125 μmol) were performed in a vacuum line by cooling the glass tube with liquid nitrogen. The loaded catalysts were kept for subsequent equilibration after 30 min in a black box.

2.3. Photocatalytic oxidation of acetaldehyde

Subsequently, the acetaldehyde-loaded F-TiO2 photocatalyts were split into four portions with 50 mg for each. They were illuminated by four surrounding lamps (NEC FL6BL-B UV-A lamps, 6W, $\lambda_{max} = 355$ nm) with 0, 20 min, 3 h, 20 h of UV illumination time, respectively. The four lamps were symmetrically positioned around the photo-reactor with a separation distance of 5 cm. This setup was housed within a UV black box which was fitted with a fan to dissipate the heat generated by the lamps, thus ensuring that the adsorption capacity was not influenced by a rise in temperature. In all cases, to record the MAS NMR spectra, the catalysts were quickly transferred to a 4 mm zirconia rotor under dry air.

2.4. Solid-state ^{13}C NMR experiments

The ^{13}C MAS NMR investigations were performed with a 4 mm Bruker MAS NMR probe on a Bruker Avance III 300 spectrometer at a resonance frequency of 300 MHz and 75 MHz for ^{1}H and ^{13}C nuclei, respectively. A 4 mm rotor and a spinning frequency of 12 kHz were used. High-power proton decoupling (HPDEC) MAS NMR spectra were recorded after an excitation with a π/2 pulse of 3.7 μs and with a repetition time of 6 s. Cross-polarization (CP) MAS NMR spectra were performed with a contact time of 2 ms and a repetition time of 4 s, respectively. Two dimensional ^{13}C-^{13}C chemical shift correlation spectra were recorded with a contact time of 1.5 ms. The ^{1}H spin-counting was carried out with a repetition time of 2 s. All the ^{1}H and ^{13}C MAS NMR spectra were referenced to tetramethylsilane (TMS). Data processing of NMR spectra was performed using the Bruker software TopSpin.

3. Results and discussion

3.1. Adsorption of acetaldehyde studied by ^{13}C MAS NMR

The high-power proton decoupling (HPDEC) and cross-polarization (CP) MAS NMR experiments were employed to explore the adsorptivity of bound molecules on the surface. With this approach, chemisorbed molecules can be easily distinguished from either physisorbed or gaseous molecules since a CP MAS NMR spectrum will be significantly influenced by the molecular mobility. Fig. 1 shows ^{13}C HPDEC and CP MAS NMR spectra of 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO2 catalyst. Upon adsorption of acetaldehyde vapor, two obvious signals at 201 ppm and 29 ppm observed in both the HPDEC (Fig. 1a) and CP (Fig. 1b) spectra, assigned to the carbonyl group and methyl group in the ^{13}C-enriched acetaldehyde bound to Ti atom, respectively. It is also noted that a broad shoulder at about 206 ppm in the CP spectrum, which could be assigned to a small portion of acetaldehyde surface species. They were strongly interacted with
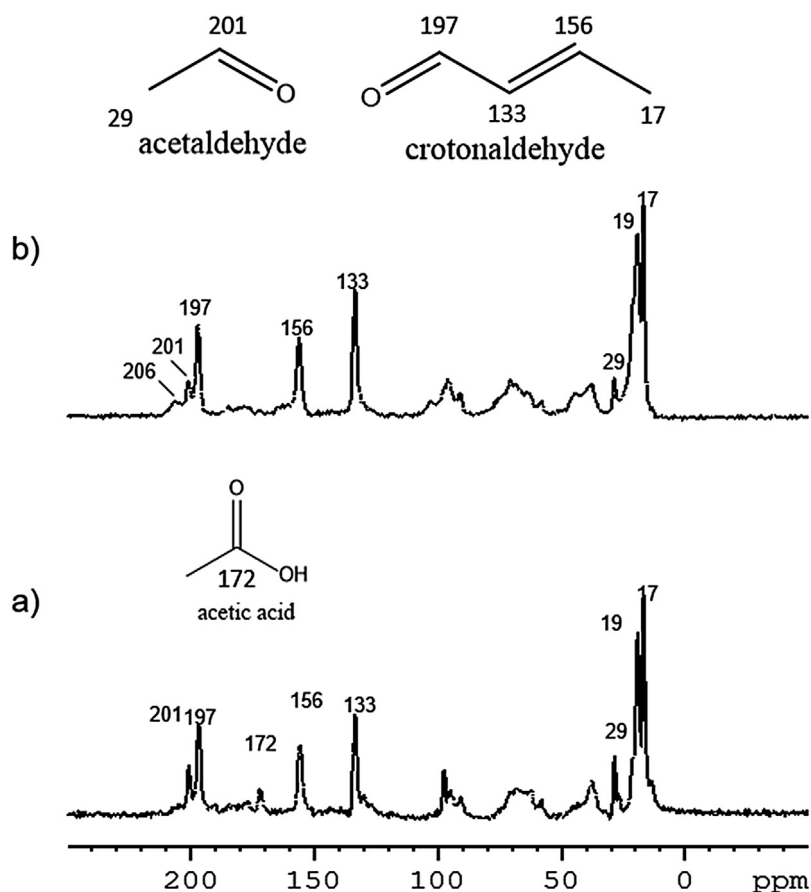
Fig. 1. ^{13}C HPDEC (a) and CP MAS NMR spectra (b) of 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO$_2$ catalyst without UV irradiation.

the surface hydroxyl groups on the F-TiO$_2$ catalyst, as CP spectrum can only detect the strongly bound molecules. In contrast, the hydrogen-bonded acetaldehyde species cannot be clearly seen in the HPDEC spectrum, which indicates hydrogen-bonded acetaldehyde species were strongly bound to the TiO$_2$ surface.

From both HPDEC and CP spectra (Fig. 1a and b), acetaldehyde were partially converted to crotonaldehyde with the characteristic chemical shifts δ = 197, 156, 133, and 17 ppm. The slight variations in the chemical shifts are very likely related to the difference in the catalyst acidity. This finding is in line with several previous studies [9–12]. Adsorption of acetaldehyde leads to spontaneous formation of crotonaldehyde without light illumination via a proton-transfer reaction, which is to large extent clarified, and believed to be facilitated by bridging hydroxyl groups possessed on the F-TiO$_2$ surface. In the previous solid-state NMR studies of acetaldehyde reaction on HZSM-5 by Haw's group [17], crotonaldehyde produced from acetaldehyde conversion on acidic zeolite HZSM-5 was observed at 353–393 K. It is also noted that a small peak occurred at 172 ppm in the HPDEC spectrum (Fig. 1a), which might be due to the formation of a small amount of acetic acid. This signal is not evidenced in the CP spectrum, which further confirms the peak assignment.

3.2. Photocatalytic oxidation of acetaldehyde studied by ^{13}C MAS NMR

The ^{13}C MAS NMR spectrum of the 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO$_2$ catalyst after UV illumination for 20 min is displayed in Fig. 2. In comparison with the spectrum recorded without any UV illumination as shown in Fig. 1, the signals with increased intensities represent species generated during the photocatalytic reaction. Meanwhile, the peaks

that are featured with decreased intensities are related to the depletion of adsorbed species. As shown in Fig. 2a, the most prominent effect of UV irradiation is the progressive depletion of chemical shifts at 201, 197, 156, 133, 98, 29, and 17 ppm. On the other hand, most of the bands with decreased intensities can be related to acetaldehyde and crotonaldehyde. It is worthy to note that after UV illumination of 20 min, a very narrow resonance at 124 ppm assigned to CO$_2$ occurred in the HPDEC spectrum (Fig. 2a), while it was not observed in the CP spectrum (Fig. 2b). The produced CO$_2$ is weakly adsorbed on the surface and supposed to be easily released. Therefore, the CP spectra did not show a narrow peak at ca. 124 ppm of the produced CO$_2$.

From the CP spectrum in Fig. 2b, with the decrease of acetaldehyde and crotonaldehyde a couple of new peaks occurred at 176, 165, and 145 ppm due to the formation of intermediate species and products rise in a parallel way. According to the previous studies reported in the literatures, [15,20–23] the resonance at 176 ppm can be assigned to the produced acetate species. The broad signal at ca. 182 ppm could be due to the formation of surface acetate species strongly bonded to the TiOH surface sites (CH$_3$COO-Ti) resulting this downfield field in agreement with the literature [24]. This assignment has been confirmed by the HPDEC spectrum recorded for this sample under vacuum at room temperature overnight as shown in Fig. 2c. Both the signals at 176 ppm and 182 ppm survived, indicating that they were rigidly adsorbed species on the F-TiO$_2$ catalyst.

The resonance at 165 ppm might be ascribed to the surface adsorbed formate species (HCOO-, formic acid minus one hydrogen ion), and the small signal at 161 ppm can be assigned to the more mobile formic acid (HCOOH). The formation of these intermediates including acetic acid acetate CH$_3$COO-Ti, formate, and formic acid
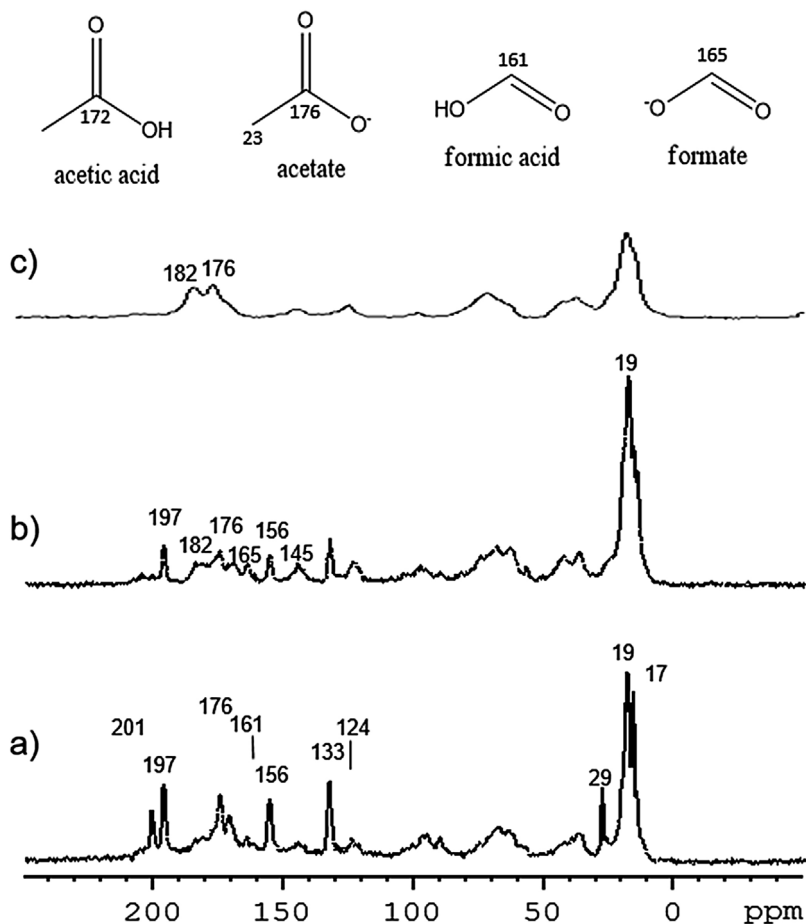
Fig. 2. ^{13}C HPDEC (a) and CP MAS NMR spectra (b) of 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO$_2$ catalyst after UV irradiation of 20 min. (c) ^{13}C HPDEC MAS NMR spectrum of 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO$_2$ catalyst after UV irradiation of 20 min and subsequently under vacuum at room temperature overnight.

are in good agreement with other studies [20,24]. The NMR lines in the range of 60–75 ppm, 35–45 ppm become more pronounced. In the absence of quantitative evaluation, the actual concentration of surface species cannot be determined. Nevertheless, the trend of variation with irradiation time can provide valuable information about the photocatalytic oxidation mechanism. The intensity of the signals of photo-generated surface species (acetate and formate) increases with irradiation time, meanwhile adsorbed acetaldehyde and crotonaldehyde complexes are progressively removed.

3.3. Complete photo-decomposition of acetaldehyde studied by ^{13}C MAS NMR

In Fig. 3, ^{13}C HPDEC MAS NMR spectra of 1, 2-^{13}C enriched acetaldehyde and oxygen adsorbed on the F-TiO$_2$ catalyst after UV irradiation of 3 h (a) and 20 h (b), respectively. Upon illumination for 3 h, the signals at 206 and 201 ppm due to acetaldehyde, and 197, 133, 98, 17 ppm assigned to crotonaldehyde eventually disappear resulting from their decomposition. Meanwhile, the signal intensity of acetate (176 ppm) and formate (165 ppm) increased since the transformation of acetaldehyde and crotonaldehyde into acetate and formate after UV light irradiation.

After prolonged irradiation up to 20 h, the carbon species on the F-TiO$_2$ surface did significantly change due to complete photo-decomposition of acetate and formate into gaseous product CO$_2$, which was continuously evolved from the catalyst surface and were detected by gas chromatograph. We have obtained clear evidence for the generation of crotonaldehyde, acetic acid, and formic

acid, along with acetate and formate complexes. From our previous study on the photocatalytic oxidation of acetaldehyde, no apparent deactivation has been observed under continuous-flow conditions. Therefore, the identified surfaces complexes do not play a significant role in poisoning of the active sites, at least in such concentrations. Furthermore, the detected adsorbed species seem to participate actively in the photocatalytic oxidation.

3.4. Two-dimensional [13]C-^{13}C chemical shifts correlation NMR spectra

In Figs. 2 and 3, both the HPDEC and CP NMR spectra in the region of 90–100 ppm, 60–75 ppm, 35–45 ppm become very crowded as a result of the formation of some unknown intermediates. They cannot be assigned unambiguously by one-dimensional experiments. Therefore, the two-dimensional [13]C-^{13}C correlation experiments (2D exchange) were applied to identify these species as shown in Fig. 4. The most important features of a 2D-NMR spectrum are the one-dimensional NMR spectra plotted along the horizontal and vertical axes, in addition to a series of peaks in the spaces between these spectra. Each of these peaks corresponds to one set of nuclear interactions. To determine which nuclei are interacting, a line is traced from the peak over to the corresponding signal on the vertical and horizontal axis spectra. This line will intersect some signals on each of the axes. These intersected signals correspond to the nuclei that are interacting as shown in Fig. 4. The identification of the intermediates and products has been confirmed by the 2D [13]C-^{13}C correlation experiments.
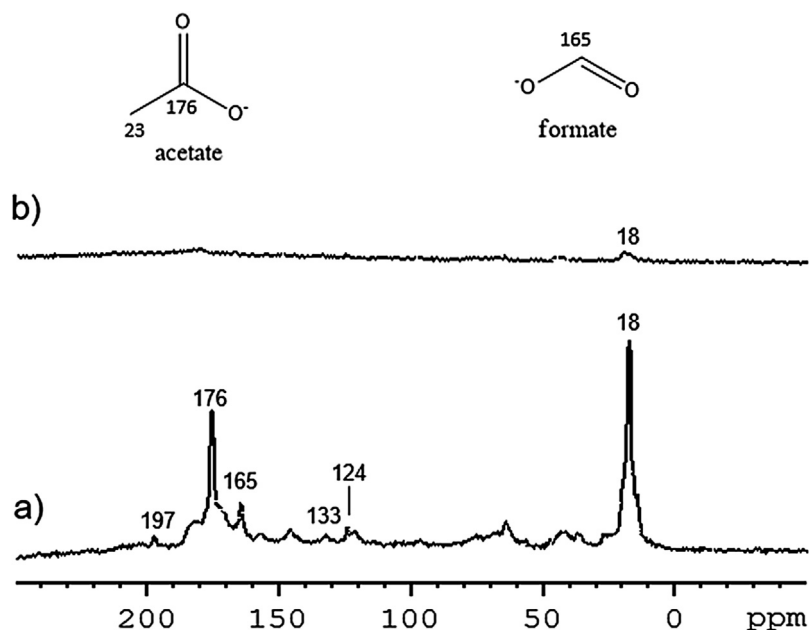
Fig. 3. ^{13}C HPDEC MAS NMR spectra of 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO$_2$ catalyst after UV irradiation of 3 h (a) and 20 h (b).
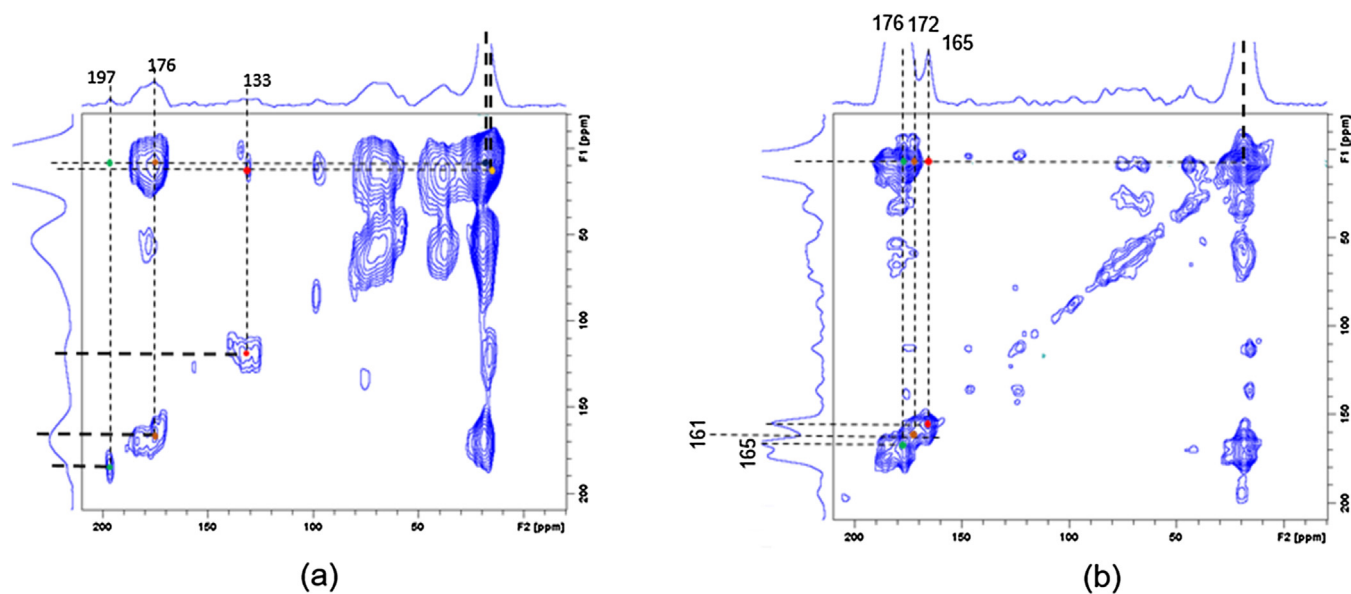

Fig. 4. Overlay of the 2D ^{13}C-^{13}C homonuclear correlation NMR spectra of 1, 2-^{13}C enriched acetaldehyde and oxygen molecules adsorbed on the F-TiO$_2$ catalyst without UV irradiation (a) and with UV irradiation of 3 h (b).

3.5. Proposed reaction pathway of photocatalytic oxidation of acetaldehyde

As we reported previously [7], the F-TiO$_2$ catalyst possesses the dominating property of acid sites on bridging titanium hydroxyl groups (TiOH) and provides negligible base sites on terminal TiOH hydroxyl groups investigated by high-field solid-state ^{1}H MAS NMR spectroscopy. It is proposed that during the flame spray pyrolysis an exchange between surface hydroxyl groups on the TiO$_2$ and fluorine atoms in the hexafluorobenzene might occur. From the photocatalytic oxidation of acetaldehyde, the F-TiO$_2$ exhibits the highest photocatalytic activity compared to the flame-made bare TiO$_2$ and benchmarking P25. It indicates that the acid sites play an important role in the aldol condensation of acetaldehyde and their complete photo-decomposition. Based on the above solid-state ^{13}C

HPDEC, CP, and 2D ^{13}C-^{13}C homonuclear correlation NMR studies, the reaction pathways involved in the adsorption of acetaldehyde on the flame-made F-TiO$_2$ catalyst, subsequent photocatalytic oxidation, and complete photo-decomposition at the presence of oxygen molecules is proposed in Scheme 1.

Firstly, acetaldehyde molecules adsorbed on titanium hydroxyl sites (Ti-OH) to form strongly bonded acetaldehyde surface species (206 ppm) and more mobile species (201 ppm). The acetaldehyde molecules are adsorbed at the bridging TiOH groups via a hydrogen bond. The formation of the hydrogen bond results in a partial charge transfer from the TiO$_2$ structure to carbonyl group and induces a change of the local charge. Then the framework oxygen at the O-Ti-O network structure intends to be more basic, resulting that the protons of the methyl group in the vicinity of this framework oxygen can be bonded via the oxygen site to form a carbanion-like
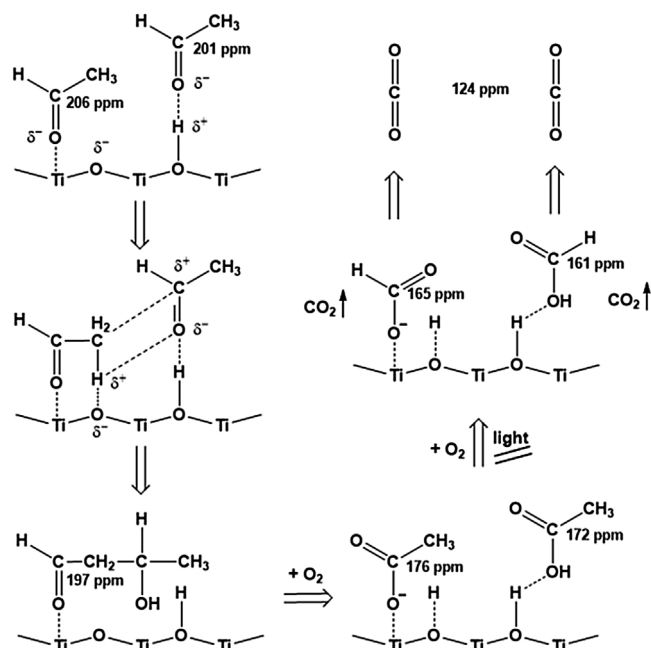
Scheme 1. Proposed reaction pathways of photocatalytic oxidation of acetaldehyde on the TiO$_2$-based catalyst.

transition state as shown in Scheme 1. Crotonaldehyde is formed via the acid-catalyzed aldol condensation. At the presence of oxygen molecules acting as an electron acceptor, the adsorbed acetaldehyde and crotonaldehyde act as electron donors and reduce the hole on the framework oxygen. Subsequent proton transfer and hydrogen abstraction lead to the formation of acetic acid and acetate species. Under UV light illumination, the formed crotonaldehyde, acetic acid, and acetate species are oxidized by the photo-generated holes or hydroxyl radicals ($^\bullet$OH). The resulting two-electron oxidation product, i.e. formaldehyde is highly reactive and further oxidized by the holes or hydroxyl radicals ($^\bullet$OH) to gaseous CO$_2$.

4. Conclusions

The present studies show that solid-state ^{13}C HPDEC, CP, and 2D ^{13}C-^{13}C homonuclear correlation NMR studies on adsorption of acetaldehyde over the flame-made F-TiO$_2$ catalyst, subsequent photocatalytic oxidation, and complete photo-decomposition at the presence of oxygen molecules. Crotonaldehyde is formed via the acid-catalyzed aldol condensation through the adsorption of acetaldehyde on the flame-made TiO$_2$ catalyst at room temperature without light illumination. At the presence of oxygen molecules as an electron acceptor, surface bonded acetaldehyde and croton-

aldehyde are completed oxidized by the transient holes in the oxygen framework generated by UV light irradiation. Solid-state NMR technique provides more detailed information on the reaction pathways of surface adsorption of acetaldehyde and its overall photocatalytic oxidation as it allows one to identify surface processes with changes of irradiation time.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.04.011.

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